



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

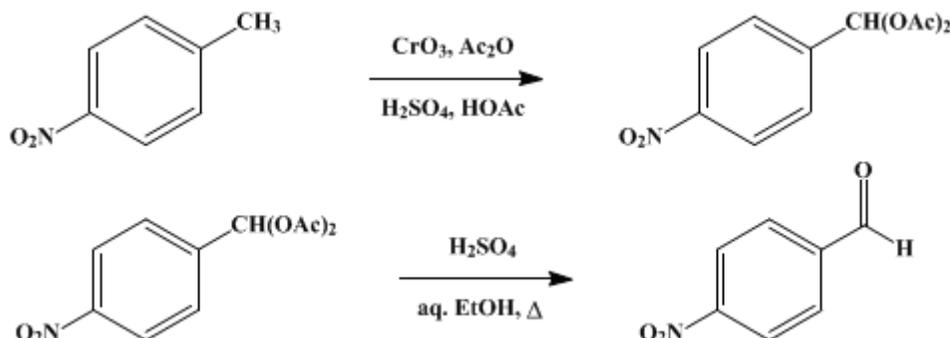
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.441 (1943); Vol. 18, p.61 (1938).

***p*-NITROBENZALDEHYDE**

[Benzaldehyde, *p*-nitro-]



Submitted by S. V. Lieberman and Ralph Connor.
Checked by John R. Johnson and E. A. Cleveland.

1. Procedure

(A) *p*-Nitrobenzaldiacetate.—In a 2-l. three-necked, round-bottomed flask equipped with a mechanical stirrer and a thermometer, and surrounded by an ice-salt bath, are placed 570 cc. (600 g.) of glacial acetic acid, 565 cc. (612 g., 6 moles) of acetic anhydride (Note 1), and 50 g. (0.36 mole) of *p*-nitrotoluene (Note 2). To this solution is added slowly, with stirring, 85 cc. (1.5 moles) of concentrated sulfuric acid (Note 3). When the mixture has cooled to 5°, 100 g. (1 mole) of chromium trioxide (Note 2) is added in small portions at such a rate that the temperature does not rise above 10° (Note 4), and stirring is continued for ten minutes after the chromium trioxide has been added. The contents of the flask are poured into two 3-l. beakers two-thirds filled with chipped ice, and cold water is added until the total volume is 5–6 l. The solid is separated by suction filtration and washed with cold water until the washings are colorless. The product is suspended in 500 cc. of cold 2 per cent sodium carbonate solution and stirred mechanically. After thorough mixing, the solid is collected on a filter (Note 5) and washed with cold water and finally with 20 cc. of cold alcohol. The product, after drying in a vacuum desiccator, weighs 44–49 g. (48–54 per cent of the theoretical amount), m.p. 120–122° (Note 6).

The crude material is suitable for hydrolysis, and for other reactions, without further purification. The pure diacetate may be obtained by recrystallizing from 150 cc. of hot alcohol. The hot solution is filtered through a fluted filter to remove insoluble impurities. The yield of pure *p*-nitrobenzaldiacetate is 43–46 g. (47–50 per cent of the theoretical amount), m.p. 125–126°.

(B) *p*-Nitrobenzaldehyde.—A mixture of 45 g. (0.18 mole) of crude *p*-nitrobenzaldiacetate, 100 cc. of water, 100 cc. of alcohol, and 10 cc. of concentrated sulfuric acid is refluxed for thirty minutes and filtered through a fluted filter, and the filtrate is chilled in an ice bath. The crystals are separated by suction filtration, washed with cold water, and dried in a vacuum desiccator. The first crop weighs 22–24 g. (82–89 per cent of the theoretical amount), m.p. 106–106.5°. A second crop amounting to 2–3 g. is obtained by diluting the filtrate with about 300 cc. of water. The total yield is 24–25.5 g. (89–94 per cent of the theoretical amount) (Note 6).

2. Notes

1. The "practical" grade of acetic anhydride (95 per cent) gave yields as high as those obtained with 99–100 per cent acetic anhydride.
2. The *p*-nitrotoluene used was a "practical" grade, m.p. 50–51°. The chromium trioxide was a u.s.p. grade of 98 per cent purity.
3. If the sulfuric acid is added too rapidly, charring occurs.

4. It is essential that the temperature of the reaction mixture be maintained below 10°. If the oxidant is added so rapidly that this temperature is exceeded, the yield is lowered considerably. With a good ice-salt bath, the time required for the addition is forty-five to sixty minutes.

5. By acidification of the [sodium carbonate](#) washings, 7–10 g. of [p-nitrobenzoic acid](#), m.p. 242–243°, is obtained.

6. This procedure appears to be generally applicable to the preparation of those substituted benzaldehydes in which the substituent is not attacked in the oxidation reaction. Thus, the submitters report that [p-bromobenzaldehyde](#) may be prepared by the same procedure, substituting 62 g. (0.37 mole) of [p-bromotoluene](#) for the [p-nitrotoluene](#) and carrying out the oxidation and isolation in the same manner. The yield of crude [p-bromobenzaldiacetate](#) is 51–64 g. (48–60 per cent of the theoretical amount), m.p. 90–92°. The pure diacetate is obtained by dissolving the crude product in 150 cc. of hot [alcohol](#), filtering through a fluted filter, and cooling. Filtration gives 39–52 g. of pure material, m.p. 94–95°. A second crop is obtained by diluting the filtrate. The total yield is 47–56 g. (46–54 per cent of the theoretical amount, based on the [bromotoluene](#)). The crude product is hydrolyzed to [p-bromobenzaldehyde](#) by refluxing 45 g. (0.157 mole) with 100 cc. of water, 150 cc. of [alcohol](#), and 10 cc. of concentrated [sulfuric acid](#), filtering through a fluted filter, cooling, and filtering with suction. A second crop is obtained by diluting the filtrate with about 300 cc. of water. The product weighs 24–28 g. (83–96 per cent of the theoretical amount), m.p. 55–57°.

It is further reported that [p-cyanotoluene](#) furnishes [p-cyanobenzaldehyde](#), the yield being about the same as that in the preparation of [p-nitrobenzaldehyde](#). (Leonard Weisler, private communication.)

3. Discussion

[p-Nitrobenzaldehyde](#) has been prepared from [p-nitrotoluene](#) by treatment with [isoamyl nitrite](#) in the presence of [sodium methoxide](#)¹ or by oxidation with [chromyl chloride](#),² [cerium dioxide](#),³ or [chromium trioxide](#) in the presence of [acetic anhydride](#).⁴ It can also be prepared by the oxidation of [p-nitrobenzyl chloride](#),⁵ [p-nitrobenzyl alcohol](#),⁶ or the esters of [p-nitrocinnamic acid](#).⁷

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 89](#)
- [Org. Syn. Coll. Vol. 3, 200](#)
- [Org. Syn. Coll. Vol. 4, 713](#)

References and Notes

1. Angeli and Angelico, *Atti accad. Lincei* (5) **8**, II, 28 (1899) (*Chem. Zentr.* **1899**, II, 371).
2. Richter, *Ber.* **19**, 1060 (1886); Law and Perkin, *J. Chem. Soc.* **93**, 1635 (1908).
3. Farbw. vorm. Meister, Lucius, and Brüning, *Ger. pat.* 174,238 [*Frdl.* **8**, 150 (1905–07)].
4. Thiele and Winter, *Ann.* **311**, 353 (1900).
5. Fischer and Greiff, *Ber.* **13**, 669 (1880); Schmidt, *Ger. pat.* 15,881 [*Frdl.* **1**, 60 (1877–87)].
6. Cohen and Harrison, *J. Chem. Soc.* **71**, 1057 (1897); Walter, *Ger. pat.* 118,567 [*Frdl.* **6**, 131 (1900–02)].
7. Baeyer, *Ger. pat.* 15,743 [*Frdl.* **1**, 60 (1877–87)].

Appendix

Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

[alcohol](#) (64-17-5)

[sulfuric acid](#) (7664-93-9)

acetic acid (64-19-7)
acetic anhydride (108-24-7)
sodium carbonate (497-19-8)
sodium methoxide (124-41-4)
p-cyanotoluene (104-85-8)
chromyl chloride
chromium trioxide (1333-82-0)
Isoamyl nitrite (110-46-3)
p-Nitrobenzaldiacetate (2929-91-1)
p-Nitrobenzaldehyde,
Benzaldehyde, p-nitro- (555-16-8)
bromotoluene (95-46-5)
cerium dioxide
p-NITROBENZOIC ACID (62-23-7)
p-Bromotoluene (106-38-7)
p-Nitrobenzyl alcohol (619-73-8)
p-Bromobenzaldehyde (1122-91-4)
p-nitrotoluene (99-99-0)
p-bromobenzaldiacetate (55605-27-1)
p-cyanobenzaldehyde (105-07-7)
p-nitrobenzyl chloride (100-14-1)
esters of p-nitrocinnamic acid (619-89-6)